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54 Process for applying a carbon-doped thin film of silicon dioxide onto a substrate

57 The invention concerns a process for applying a carbon-doped thin film of silicon dioxide onto a substrate and one or several reaction gasses containing carbon, silicon and oxygen is introduced into the chamber containing the substrate and a chemical deposition from the gaseous phase is undertaken and in the chamber a plasma is produced with a density of greater than  $10^{16}$  ions/m<sup>3</sup> containing a large number of dissociated components of the reaction gasses and

the components are forced to circulate onto the surface of the substrate.

## Description

The invention concerns a process for applying a carbon-doped thin film of silicon dioxide onto a substrate based on the preamble of Claim 1.

Insulating thin layers of silicon dioxide are used in semiconductor devices in order to insulate electric compounds in an even plane or between various planes. The denser the wrong connection, the more frequently parasitic couplings occur, however which impair performance. For this reason insulating layers with low dielectric constants are desirable.

Pure silicon dioxide films have a dielectric constant of about  $k = 4$  and are usually produced by oxidizing pure silicon using  $O_2$  or  $H_2O$  gas or they are supported by chemical deposition from the gaseous phase, if necessary plasma, and as reaction gas one may use gas mixtures such as  $SiH_4/Ar/N_2O$ ,  $SiH_4/Ar/NO$  and/or  $SiH_4/Ar/O_2$  as reaction gasses. Chemical deposition from the gaseous phase is used mostly for the intermediate compound dielectrics.

It is well known how to incorporate fluorine into the silicon dioxide matrix in order to lower the dielectric constant with the result being an  $F_xSiO_4$  matrix. Here within the context of the chemical deposition from the gaseous phase  $SiF_4$  is used in the mixture as reaction gas together with silane and oxygen. By means of this the dielectric constant can be reduced to about  $k = 3.5$ . Lower values cannot be achieved due to the stability of the thin film and because of moisture absorption problems.

It is also well known how to use a centrifugal coating in order to obtain a carbon-containing  $SiO_2$  with a dielectric constant of about  $k = 3.0$ . Although such thin films are suitable for a good many applications including for intermediate compound dielectrics, this process has

numerous preparation disadvantages. Thus, this requires the use of liquids and it produces waste materials which have to be disposed of. Frequently films with high  $\text{OH}^-$  concentrations are produced. In addition, such thin films are frequently unstable with respect to temperature, they have low tensile strength, they are burdened with moisture adsorption/desorption problems. Aside from that, many manufacturers prefer the chemical deposition from the gaseous phase.

Consequently it is well known how to produce organically doped silicon dioxide films by means of chemical deposition from the gaseous phase and how to use as precursor substances methyl silane ( $\text{CH}_3\text{-SiH}_3$ ) or phenyl silane ( $\text{C}_6\text{H}_5\text{-SiH}_3$ ) as a substitute for the silane precursor. The methyl or phenyl group is only partly dissociated where a few of the methyl or phenyl components remain bonded to the silicon atom in the silicon dioxide film. Thanks to this, a dielectric constant of about  $k = 3$  is achieved. It is also well known how to use  $\text{CH}_3\text{-SiH}_3$  together with  $\text{H}_2\text{O}_2$ . Such organically doped silicon dioxide films which are produced by chemical deposition from the gaseous phase frequently have low adhesion and moisture absorption and temperature stability problems.

It is also well known how to use thin films of organic polymers, for example polyimids, polyethyl ethers, etc. which have a very low dielectric constant of  $k = 2.5$ . However, with respect to their integration, these substances are problematic.

During plasma-supported chemical deposition from the gaseous phase (PE-CVD) the reaction gases are partly dissociated in the plasma as a result of the collisions with electrons and other molecules and radicals. Nevertheless, many carbon atoms remain bonded to oxygen, silicon, hydrogen and other carbon atoms during the deposition process. In an undesirable way, many of the carbon atoms remain bonded to these components even after adsorption to the

substrate and incorporation into the silicon dioxide films. These carbon atoms are not finely distributed and isolated in the  $\text{SiO}_2$  matrix so that the quality of the thin film is not optimal. With plasma-supported chemical deposition a series of reaction gasses is used including tetraethylorthosilicate (TEOS or  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), methyl trimethoxysilane (MTMS or  $\text{SiCH}_3(\text{OC}_2\text{H}_5)_3$ ) and phenyltrimethoxysilane (PTMS or  $\text{SiC}_6\text{H}_5(\text{OC}_2\text{H}_5)_3$ ). Oxide deposition which uses highly diluted TEOS/ $\text{O}_2$  and precursors such as  $\text{Si}(\text{OC}_2\text{H}_5)_n(\text{OH})_{4-n}$  and  $\text{Si}(\text{OC}_2\text{H}_5)_n\text{O}_4$ ,  $n$  has  $n = 0-3$ , was produced with good deposition results since with it good adhesion properties are obtained. Similar results are obtained in conjunction with PTMS. However, the presence of carbon leads to undesirable hydrocarbon fragments in the resulting layer of oxide and to poor tensile strength properties of the thin film. The plasma used during the plasma-supported chemical deposition has a relatively low density and results in C-H bonds as can be seen from Figures 1 and 2 which give infrared spectra for an  $\text{SiO}_2\text{C}_x$  thin film which was produced by chemical deposition from the gaseous phase or by centrifugal coating. Both spectra show significant peaks at  $781\text{ cm}^{-1}$  and  $1027\text{ cm}^{-1}$ . The height of these peaks additionally shows that the carbon atoms are not isolated in the  $\text{SiO}_2$  matrix, as desired, rather they are bonded to hydrogen atoms which were not dissociated during the deposition.

The problem of the invention is to create a process based on the preamble of Claim 1 which makes it possible to produce a thin layer with a low dielectric constant.

This problem is solved according to the characterizing portion of Claim 1.

Thanks to this dielectric constants can be achieved in the range from  $k = 2.5$  to  $3.5$  and especially in the range from  $k = 2.9$  to  $3.2$ . In the  $\text{SiO}_2\text{C}_x$  thin film there is additionally a reduction of the number of  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  radicals which are bonded to the carbon atoms by means

of which improved thin film properties are produced with respect to tensile strength and thermal stability. A minimum number of "dangling" bonds is obtained. The carbon atoms are finely distributed in the amorphous silicon dioxide matrix and thus result in the very low dielectric constant.

Additional embodiments of the invention are to be found in the following description and subclaims.

In the following the invention will be described in greater detail in conjunction with the attached figures.

Figure 1 shows an infrared spectrum of an  $\text{SiO}_x\text{C}_y$  thin film which had been produced by chemical deposition from the gaseous phase.

Figure 2 shows an infrared spectrum of an  $\text{SiO}_x\text{C}_y$  thin film which had been produced by centrifugal coating.

Figure 3 shows schematically a device for producing a thin film using a highly dense plasma.

The device illustrated in Figure 3 for the chemical deposition from the gaseous phase using a highly dense plasma (HDP-CVD, High Density Plasma Chemical Vapor Deposition) comprises a central chamber 2 in which the semiconductor or insulator substrates 4 sit on a boat which does not harm substrates 4 or introduce any sort of impurities into substrates 4. Boat 6 preferably consists of graphite or quartz. Central chamber 2 consists of a material which is capable of resisting pressures of less than 1 mTorr or less, is minimally out-gassed at such pressures and it does not create any impurities which penetrate the inside of chamber 2 or substrates 4 or a thin film located thereon. Chamber 2 preferably consists of a ceramic material.

however a metal such as stainless steel or aluminum may also be used. Central chamber 2 operates at an operating pressure which is much lower than in ordinary chambers for chemical deposition from the gaseous phase or plasma-supported chemical deposition from the gaseous phase. The pressure within chamber 2 is preferably 5 mTorr, whereas with plasma-supported chemical deposition from the gaseous phase typically a pressure of about 2 Torr is used. The density of the plasma within chamber 2 is much higher than in the normal chemical deposition from the gaseous phase even if it is plasma supported and it is preferably above  $10^{16}$  ions/m<sup>3</sup>, preferably in the range from  $10^{16}$  to  $10^{22}$  and especially in the range  $10^{17}$  to  $10^{19}$  ions/m<sup>3</sup>. The density of the plasma could also be higher, however. In comparison to this at the typical operating pressure of a chamber for plasma-supported chemical deposition from the gaseous the plasma density lies within the range from  $10^{14}$  to  $10^{16}$  ions/m<sup>3</sup>.

Electromagnetic energy is introduced by producing preferably a linear or almost linear electric field or a B magnetic field. The electromagnetic field is enough to increase the dissociation of the reaction partner and oxidation gasses considerably within chamber 2. The applied electromagnetic field causes the increased dissociation by producing a high-energy plasma within chamber 2. A high dissociation energy caused by the electromagnetic field and fast-moving electrons and ions within chamber 2 as well as the density of the plasma itself result in increased collisions which produce molecules, ions, elements and/or radicals which are components of the reaction gas which was initially introduced into chamber 2.

Thanks to the high ion density of the plasma within chamber 2 and the electromagnetic field a very high number of successful dissociation reactions are achieved between ions and molecules. Although the free path is determined by the pressure, the yield of dissociation

reactions is typically produced by using a magnetic field thanks to which larger paths of the ions are brought about before they are captured on the electrode. Accordingly, the high ion density of the plasma along with the magnetic field causes a larger total number of collision to occur between reaction participants, components and ions within the plasma. The degree of dissociation of the reaction participants and components in the plasma is increased by this since each ion experiences more collisions along its path before it is adsorbed on the substrate 4.

The total number of collisions in the illustrated device is especially increased by the fact that the applied magnetic field forces the reaction participants and components to move circularly, spirally or helically. This spiral movement increases the paths by means of which the total number of collisions increases and the degree of dissociation within chamber is increased considerably.

The magnetic field is preferably produced by a current-carrying coil which extends linearly and homogeneously along the length of chamber 2. Charged electrodes, ions and radicals are conducted spirally as a result of the electromagnetic field. These fast-moving, charged particles collide with the reaction participants and break these latter up and the oxidation gasses, if they are introduced into chamber 2, produce simpler ions and radicals. Under optimum conditions the dissociation in chamber 2 proceeds to such an extent that a large number of particles, after they were subjected to plasma conditions over their paths, are elementary and electron components of the reagent.

Substrates 4 are preferably silicon wafers, however they may also consist of any other semiconductor or insulation material. The silicon wafers may be of the p- or n-type, doped or undoped and they have differing concentrations of doping agent. The wafers may be polished or



unpolished. The wafers may consist of untreated, doped or undoped material or they may be partly treated.

One or several reaction gasses may be introduced into chamber 2 though one or several inlet openings 8. The introducing of any reaction gas is controlled separately by gas flow valve 10 so that specific mixtures of reaction gasses can be introduced into chamber 2 in order to maximize the application conditions. Chamber 2 is also controlled by a valve so that the suitable gas mixture is achieved in chamber 2.

A few preferred reaction gasses which may be used are methane ( $\text{CH}_4$ ) and silane ( $\text{SiH}_4$ ), tetraethylorthosilicate (TEOS or  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), methyl trimethoxysilane (MTMS or  $\text{SiCH}_3(\text{OC}_2\text{H}_5)_3$ ) and phenyl trimethoxysilane (PTMS or  $\text{SiC}_6\text{H}_5(\text{OC}_2\text{H}_5)_3$ ). What is common to these is that they all contain carbon and silicon. Other reaction gasses may be used which contain either carbon and silicon or one of these elements or none thereof, however it is preferred that they contain either a reaction gas or a combination of reaction gasses of carbon and silicon. If the reaction gasses do not contain any oxygen as is the case with the combination of methane and silane, it is preferred introducing an oxidation gas into chamber 2 separately together with the reaction gasses. Preferred oxidation gasses include  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ . After dissociation of the reaction gasses in the plasma carbon is introduced into the amorphous silicon matrix and oxygen reaches the substrate surface. Together with the just-mentioned reaction gasses an oxidation agent and a dilution gas are preferably introduced into chamber 2.

Non-reacting gasses may also be introduced into chamber 2 and they act as initiators in order to facilitate and promote ionization and dissociation within the plasma for the reaction gasses. It is preferred using only inert gasses such as argon since in contrast of the chemical

deposition from the gaseous phase, plasma-supported or not, diatomic dilution gasses such as  $H_2$  or  $O_2$  may be easily dissociated in chamber 2 and then bond with the carbon atoms or other components within the resulting thin film on substrate 4 since the degree of dissociation is correspondingly increased in chamber 2 because of the highly dense plasma.

If the reaction gasses inside chamber 2 are exposed to the magnetic and/or electric field as well as to constant bombardment by electrons as well as ions and radicals then chamber 2 and substrate 4 become very hot due to the absorption of hot components from the plasma. Temperatures of  $400^\circ C$  or more may occur in chamber 2 and in substrate 4. Because of this, it is frequently necessary to heat substrate 4 further in order to increase the surface reactivity. Substrate 4 may be heated by arranging it within furnace 12 with a furnace control 13 or bombarding it with electrons or photons.

Corresponding to a predetermined composition reactions gasses, oxidation gasses and dilution gasses are introduced into chamber 2 in which highly dense plasma is produced using electromagnetic fields and the dissociated components of the reaction gasses are forced to circulate onto the surface of substrate 4. The rate at which the gaseous reaction participants and their dissociated components reach the substrate surface depends on the mass transport properties of the plasma and is only slightly temperature dependent. The chemical deposition using a highly dense plasma gives attractive gaseous phase concentrations and consequently corresponding thin films.

The dissociated components of the reaction gasses are moved circularly in order to approach substrate 4. The components are located on the substrate if an adsorption can take place easily. Before an adsorption takes the components occupy a position adjacent to the

substrate which is near enough to the substrate so that a dipol-dipol or ion reciprocal reaction may take place between the components and the atoms on the substrate surface with sufficient probability so that the components are bonded to the surface. In so doing, collision may take place possibly between the components and the substrate surface.

On the boundary between plasma and substrate an adsorption takes place of gaseous components of the reaction gas and of the oxidation gas if this latter is introduced into chamber 2, adsorption generally takes place if an atom or molecule appears on the surface and loses enough energy on the components of the surface in order to be bonded. Chemical absorption takes place if electrons are exchanged and ionic forces stop the atom or molecule.

Once adsorbed, the atoms and ions migrate along the surface and react in order to form a thin film on the surface of the substrate. During chemical deposition from highly dense plasma, a high degree of element adsorption is anticipated based on the high degree of dissociation. In this way fewer of the carbon-bonding positions are occupied by undesirable radicals such as H and OH since the carbon atoms are very free of these bonded radicals during adsorption on the surface. The desired effect of the reduction of the number of "dangling" bonds within the film is likewise a result of using a highly dense plasma. The carbon atoms then occupy a position in the glassy matrix which otherwise would be occupied by silicone atoms in the purely amorphous  $\text{SiO}_2$ . That is to say, the carbon atom preferably occupies a position to which each of its four bonding points an oxygen atom is bonded. After the adsorption and reaction processes the gaseous by-products of the surface reactions are desorbed and removed from chamber 2.

Based on the applied, highly dense plasma carbon and silicon atoms are liberated from radicals by means of which an increased thermal stability of the resulting dielectric thin film is

achieved. Moreover, the free silicon, oxygen and carbon atoms may be adsorbed on the surface of the substrate and they may react free from radicals located thereon so that there is a smaller number of positions with C-H bonds, an all together lower hydrogen content and a lower silanol content in the resulting dielectric thin film.

The use of methane/silane, TEOS, PTMS and/or MTMS as reaction gasses is preferred since in each case they contain carbon. Inside chamber 2 the carbon atoms dissociate from other molecular components of the reaction gas. The carbon atoms then become important components of the oxidic thin film. The presence of the carbon atoms in the resulting thin film reduces the dielectric constant of the thin film to about  $k = 2.9$  to  $k = 3.2$ . The carbon atoms do not attack the substrate or the components of the thin film and they do not have a corrosive effect either regardless of whether they are combined with hydrogen or not.

Carbon-doped silicon dioxide films are advantageous with respect to  $\text{SiO}_2\text{F}_x$  films which were likewise produced from a highly dense plasma and they have lower dielectric constants than typical  $\text{SiO}_2$  films do. Fluorine atoms may attack the bonding materials during a subsequent treatment at increased temperature.

#### Patent Claims

1. Process for applying a carbon-doped thin film of silicon dioxide onto a substrate and one or several reaction gasses containing carbon, silicon and oxygen is introduced into a chamber containing the substrate and a chemical deposition from the gaseous phase is undertaken, characterized by the fact that in the chamber a plasma is produced with a density of more than  $10^{16}$  ions/ $\text{m}^3$  containing a number of dissociated components of the reaction gasses and the

components are forced to circulate onto the surface of the substrate.

2. Process based on Claim 1, characterized by using one or several reaction gasses selected from the group consisting of

- (1) methane and silane.
- (2) tetraethylorthosilicate (TEOS).
- (3) methyl trimethoxysilane (MTMS), and
- (4) phenyl trimethoxysilane (PTMS).

3. Process based on Claim 1 or 2, characterized by the fact that in addition to the reaction gasses inert gas is introduced into the chamber.

4. Process based on one of Claims 1 through 3, characterized by the fact that energy is introduced into the surface of the substrate in order to facilitate chemical reactions of components adsorbed on the substrate surface.

5. Process based on Claim 4, characterized by heating the substrate by means of a source of heat while the reaction components circulate close to the substrate.

6. Process based on Claim 4, characterized by introducing the energy by bombarding the surface of the substrate with energy particles while the components are circulating close to the substrate.

7. Process based on one of Claims 1 through 6, characterized by desorbing the gaseous by-products from the chamber.

8. Process based on one of Claims 1 through 7, characterized by keeping the chamber at a pressure of less than 100 mTorr.

9. Process based on Claim 8, characterized by keeping the chamber at a pressure of less than 25 mTorr.

10. Process based on one of Claims 1 through 9, characterized by adjusting a plasma density within the range from  $10^{16}$  to  $10^{22}$  ions/m<sup>3</sup>.

11. Process based on one of Claims 1 through 10, characterized by introducing an oxidation gas into the reaction gasses in the chamber.

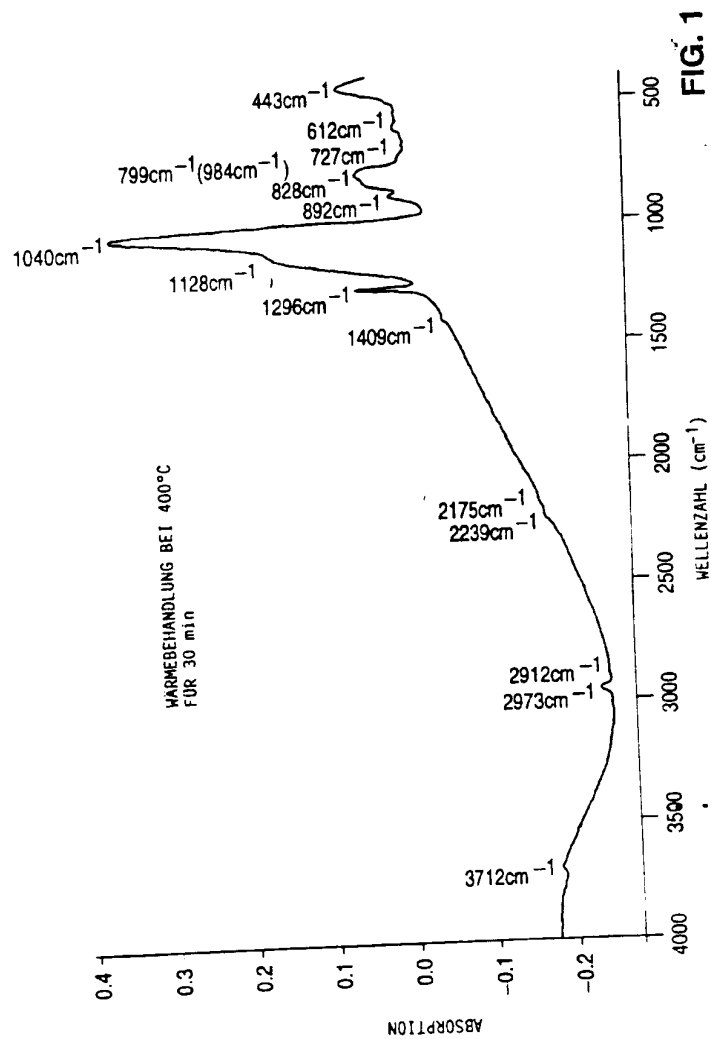
12. Process based on Claim 11, characterized by using O<sub>2</sub> and/or H<sub>2</sub>O<sub>2</sub> as oxidation gas.

13. Semiconductor component with a semiconductor substrate and at least an SiO<sub>2</sub>/C<sub>1</sub> thin film, characterized by the thin film having a dielectric constant between 2.5 and 3.5 and especially between 2.9 and 3.2.

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Attached 3 pages of Drawings

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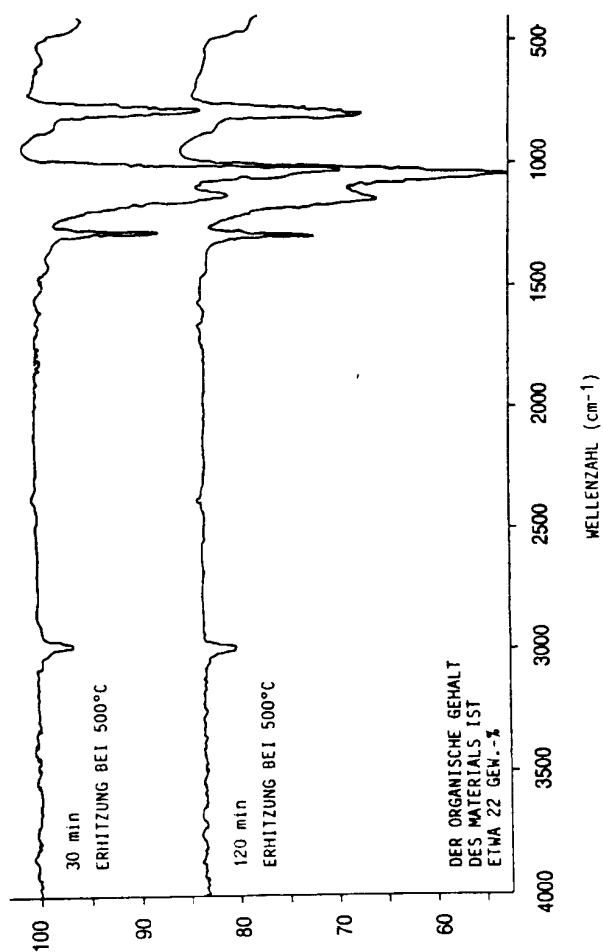
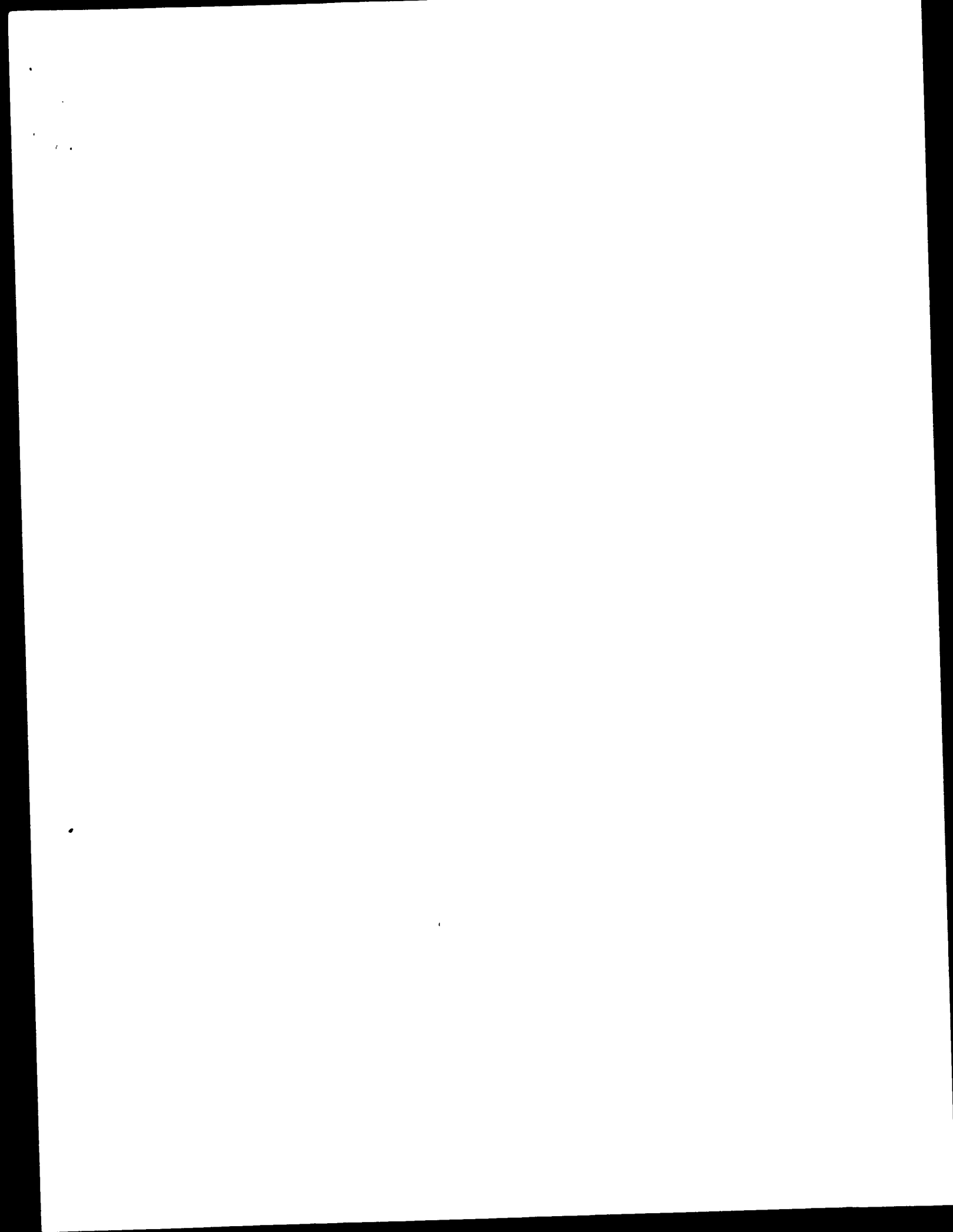


FIG. 2





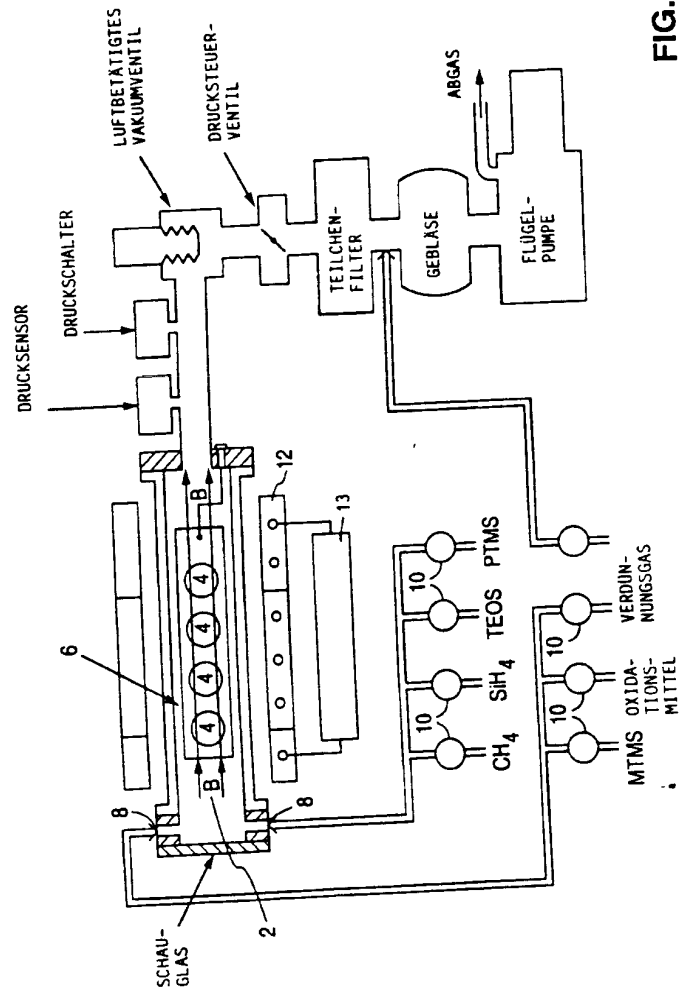


FIG. 3